

Standard Operating Procedure for Analysis of Mercury in Precipitation

**Gerald J. Keeler and Matthew S. Landis
University of Michigan
Air Quality Laboratory
109 South Observatory Street
Ann Arbor, MI 48109-2029**

June 1, 1994

Version 2.0

Standard Operating Procedure for Analysis of Mercury in Precipitation

1.0 Introduction/Overview

The objective of the Lake Michigan Loading Study is to assess the contribution of atmospheric deposition to the concentration of mercury and other toxic trace species found in Lake Michigan. The atmosphere has been implicated as one of the dominant sources of mercury and trace elements to bodies of water and it is clear from investigations in remote regions of the globe that long range transport of mercury and other toxics from source regions is occurring. By quantifying the wet deposition and ambient concentrations of mercury it will be possible to determine the relative importance of precipitation and dry deposition in accounting for the atmospheric loading of mercury to Lake Michigan. In addition, investigating other ambient trace species will aid in the identification of significant mercury sources.

2.0 Sample Handling and Processing

2.1 Sample Handling

Precipitation samples contain exceptionally low levels of trace metals and therefore these samples are processed with careful attention to avoid contamination. Blanks are routinely analyzed to ensure extremely low analyte levels and operating conditions.

When samples are received at UMAQL they are logged in, the tracking form sent with the sample is catalogued and the sample is taken to a staging area to be moved into the clean room. At the staging area outside the clean room, the outer polyethylene bag is removed from the sample. The double-bagged sample is placed in the outer room of the clean room, and the analyst suits up to enter the clean room according to laboratory protocol. As the sample is brought into the clean room the second outer bag is removed and left in the outer room of the clean room. The inner bag is removed inside the clean room and discarded.

2.2 Sample Processing

The precipitation volume of each sample is determined gravimetrically. Mercury samples are oxidized to 1% bromine monochloride volume/volume and are stored in a dark cold room overnight before being analyzed according to the following procedure.

3.0 Sample Analysis and Data Acquisition

3.1 Summary

Mercury is purged from solution in a mercury-free nitrogen stream after appropriate sample pretreatment and reduction. Mercury liberated from solution is concentrated on a gold-coated bead trap. A mercury-free pretreated soda lime trap is utilized in the purge system to capture acid gases

that may damage the gold-coated bead trap. The gold-coated bead trap is subsequently thermally desorbed and carried by a mercury-free helium stream into a cold-vapor atomic fluorescence (CVAFS) analyzer where the mercury atoms are excited by light of wavelength 253.7 nm. These excited atoms fluoresce in the same wavelength which is detected by a photomultiplier tube and the signal is converted to voltage which is sent to an integrator.

All analytical procedures for determination of mercury in precipitation are carried inside a Class 100 Clean Room. Volatilization/Recapture (Section 3.3.1) is carried out in a class 100 laminar flow exhaust hood inside the clean room. Nitrogen utilized for purging is 99.998% pure and is stripped of any mercury using a gold coated trap before use in the purge system. Clean room gloves are worn at all times and all labware with which the samples and reagents comes into contact is cleaned weekly using the acid cleaning procedure described in *Standard Operating Procedure for Sampling of Mercury in Precipitation*, Section 2.1.

3.2 Reagents and Materials

All reagent lot numbers, preparation dates and procedures are recorded for each new batch of reagent used. A reagent blank is obtained after each new batch of reagent has been prepared. Bromine monochloride (BrCl), stannous chloride (SnCl_2) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) are prepared fresh monthly.

Solid reagents (potassium bromide, potassium bromate, hydroxylamine hydrochloride and stannous chloride) are stored in the clean room in a desiccator containing silica gel and an open bed of activated charcoal. The caps of all reagent bottles are Teflon taped to reduce entry of vapor phase compounds. Even with these precautions, reagents will nevertheless absorb mercury over time and must be replaced. All reagents are made in the clean room, except the working standard solution.

3.2.1 Hydrochloric Acid

EM Science Suprapur hydrochloric acid is used to prepare BrCl and SnCl_2 . This acid characteristically has a very low blank value (20 pg/mL).

3.2.2 Bromine Monochloride

Bromine monochloride is prepared in a class 100 laminar flow exhaust hood by adding 11.0 mg KBr per mL of HCl while the solution is stirred using an acid-cleaned Teflon-coated magnet stirrer. When the KBr is dissolved, 15.0 mg KBrO_3 per mL of HCl is added slowly and the solution is allowed to continue stirring. This process produces chlorine and bromine gas and must be performed slowly in a functioning fume hood. After addition of the salts the solution is a deep yellow color. If there is no color (or very faint) then the BrCl has been substantially reduced and will not have enough oxidizing power for use. In this case, the solution is remade. Bromine monochloride is stored at room temperature in the clean room. Fresh bromine monochloride is prepared monthly or as needed.

3.2.3 Hydroxylamine Hydrochloride

30 grams of $\text{NH}_2\text{OH}\cdot\text{HCl}$ is dissolved in MQ-water to make 100 mL in an acid-cleaned 100 mL volumetric flask. This solution is purified by adding 0.5 mL of SnCl_2 and purging overnight with Hg-free N_2 . The solution is stored in an acid-cleaned, dark Teflon bottle in the refrigerator. Fresh hydroxylamine solution is prepared every month or as needed.

3.2.4 Stannous Chloride

20.0 grams of $\text{SnCl}_2\cdot\text{H}_2\text{O}$ is placed into an acid-cleaned 100 mL volumetric flask. Working in a fume hood, 10 mL of concentrated HCl is added and the solution is then brought to 100 mL with Milli-Q water. The solution is stored in an acid-cleaned, dark Teflon bottle in the refrigerator. Fresh stannous chloride is prepared every month or as needed.

3.2.5 Milli-Q Water

Deionized water, with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$, is prepared using a Milli-Q system from a pre-purified (reverse osmosis) water source. Milli-Q water is used for reagent preparation.

3.2.6 Soda Lime Traps

High purity grade soda lime (EM Science) is utilized in an acid-cleaned glass tube with glass wool endplugs and Teflon connectors. After packing, this trap is conditioned by purging a 0.5 M HCl solution through the trap for 30 minutes. The soda lime trap is changed after analysis of 30 samples.

3.2.7 Preparation of Working Standard Solution

100 μL of the stock Hg solution (1 mg/mL in nitric acid) is pipetted into a 1 L volumetric flask. 5 mL of concentrated BrCl is added and the flask is brought up to volume with MQ-water and thoroughly mixed. This is the Secondary Standard solution (100 ng Hg/mL). Replace this solution as needed (it is stable for at least one year).

The Working Standard (2 ng Hg/mL) is prepared from the Secondary Standard solution by placing 2 mL of Secondary Standard into a 100 mL volumetric flask, adding 1 mL of BrCl and bringing the solution to volume with MQ. The Working Standard is replaced monthly.

3.3 Sample Analysis and Data Acquisition

3.3.1 Volatilization/Recapture

Volatilization of mercury from solution is accomplished using a glass impinger assembly manufactured at the University of Michigan. A 100 mL graduated bubbler attaches to an impinger via a ground glass fitting. N_2 flow is regulated using a Teflon stopcock. A soda lime trap is incorporated into the system to prevent damage of the gold-coated bead traps by capturing acid gases liberated during the purging procedure.

Total mercury is quantified by oxidizing all mercury forms using bromine monochloride. Bromine monochloride is a strong oxidizing agent, capable of breaking organic bonds with mercury, thus liberating the divalent form of mercury. Approximately 10 mL of the oxidized precipitation sample to be analyzed is poured into an acid-cleaned or previously purged glass bubbler. The bubbler is rinsed by gently swirling the solution. After rinsing, the solution is discarded. 100 mL of the oxidized precipitation sample is carefully poured into the graduated glass bubbler and 250 μ L of hydroxylamine hydrochloride is added. A stopper is then inserted into the bubbler, its swirled briefly and allowed to react for 5 minutes to reduce the excess bromine monochloride from solution. Bromine monochloride is reduced from solution since halogens liberated from solution will quickly damage the gold-coated bead traps onto which the purged elemental mercury is amalgamated.

A blanked gold-coated bead sample trap is affixed to the end of the soda lime trap. The bubbler is opened, 500 μ L of stannous chloride is added, and the bubbler is quickly attached to the impinger. The N₂ flow is adjusted to 450 cc/min using a calibrated rotameter and the solution is purged for 7 minutes. The stannous chloride reduces the divalent mercury to Hg⁰ which is quantitatively captured on the gold-coated bead trap.

3.3.2 Analysis of Total Mercury

The CVAFS analyzer used for mercury in precipitation determinations is kept on at all times, since this has been shown to stabilize the UV lamp and maintain consistency from one day to the next. The power supplied to the CVAFS analyzer is modulated by a line tamer (Shape Magnetronics) to prevent power fluctuations. It is imperative that the mercury lamp not experience wide temperature fluctuations or power surges since both of these drastically affect the sensitivity of the instrument. During operation of the instrument the helium carrier gas flow rate is regulated upstream of the analyzer using a mass flow controller (Tylan) which is set to maintain a 35 cc/min flow rate. This flow rate has been determined by UMAQL to yield the optimal peak characteristics for mercury standards. The regulator on the helium cylinder is set at 50 Kilopascals. The helium stream is prefiltered using a gold-coated trap before entering the analytical train in order to remove any mercury. In the analytical train, mercury is thermally desorbed from the sample trap, and amalgamated onto the analytical trap which is subsequently thermally desorbed into the CVAFS analyzer where the mercury atoms are detected. Traps are desorbed by heating a nichrome coil which is wrapped around the trap covering the gold-coated beads. Application of 12 volts of current to the coil is sufficient to achieve a temperature of 500°C inside the gold bead trap (voltage may vary due to variations in length and thickness of nichrome wire). Two fans supply cool air to the sample and analytical trap separately in order to speed analysis time.

For comparability between laboratories UMAQL sets the gain on the CVAFS analyzer to yield an approximate 1000 mV net response for a 1 ng mercury standard. The background on the CVAFS analyzer is set at 5.0 and maintained in that position in order to track the drift in the baseline of the analyzer. A Hewlett Packard Integrator is connected to the analyzer to convert output signal into an integrated area of the detected response. Area units (AU) are used for all sample calculations since area is much more reliable than peak height.

To analyze a sample trap, the trap is placed snugly into the analytical train using friction fit Teflon connectors and Teflon sleeves. The nichrome coil used specifically for the sample trap is slid over the trap and moved to completely cover the quartz wool plugs and the gold-coated beads contained between the plugs. Helium is allowed to flow through the sample trap for 2 minutes before analysis begins in order to purge air and water vapor from the analytical train. A circuit controller (ChonTrol) is employed which is programmed to turn on the variable transformers and fans in a precise and reproducible manner. First, the sample coil is heated for 2 minutes, then it is cooled while the analytical trap is heated for 2 minutes. The analytical trap is then cooled for 2.5 minutes and the fan to the sample trap is turned off. While the analytical trap is cooling, a new sample trap is installed in the analytical train and helium is passed through this trap until the analytical trap is cool and ready for another sample. When the analytical trap begins heating, the integrator is turned on and the ambient temperature, time and base mV are recorded in a log book and the LCD display on the analyzer is set to record the peak mV (by depressing the Peak button on the face of the analyzer). After the sample is analyzed and the peak height and area reported by the CVAFS and integrator respectively, these values are recorded in the log book.

A standard curve is analyzed at the beginning of each day of analysis and a control standard which yields a response in the range of the samples being analyzed is run every six samples. Criteria for the standard curves and control standards are described below in Section 3.3.4. All sample analysis is recorded in a log book specific to the analyzer with which samples are being quantified and also in a lab notebook specific to the study for which the samples were collected. At the end of the day of analysis all results from the log sheet are entered into a computer spreadsheet file for subsequent checking and processing by a statistical software program, SAS (Cary, NC).

3.3.3 System Purge and Blanks

At the start of each day of analysis, each impinger system is purged after the soda lime trap is conditioned. First 25 mL of Milli-Q water is added to an acid cleaned bubbler, then 1.0 mL of SnCl_2 is added and the solution is purged at 450 cc/min for 15 minutes. After each system is purged a System Blank is generated to ensure the impinger assembly is free of contamination.

System Blank (Bubbler Blank): This blank is generated by adding 1.0 mL of SnCl_2 to the system purge solution and purging the solution onto a blanked gold-coated bead trap at 450 cc/min for 5 minutes. After the System Blanks have been completed, one of the purged bubblers is dedicated for generation of standards.

A Total Reagent Blank is generated on each day of analysis for each analytical aliquot volume. The Total Reagent Blank is used to calculate the method detection limit (presently 0.1 ng/L for a 100 mL aliquot) and to calculate sample concentration (Section 3.3.5).

Total Reagent Blank: A Total Reagent Blank is generated in sample solution that has been purged of mercury. Bromine monochloride is pipetted into the solution, allowing reduction of halogens by hydroxylamine for 5 minutes then mercury is purged from the solution after adding SnCl_2 . Purged mercury is captured on a gold-coated trap and analyzed as described above in Section 3.3.2. For a 100 mL aliquot the following reagent volumes are used: 1.0 mL of BrCl , 0.25 mL $\text{NH}_2\text{OH}\cdot\text{HCl}$, and 0.5 mL of SnCl_2 .

3.3.4 Standard Curve and Control Standards

A standard curve, generated by bubbling different volumes of mercury working standard solution, is analyzed before each day of analysis. The amount of mercury bubbled for the calibration curve is tailored to the expected value of the samples to be analyzed. At UMAQL, a typical calibration curve consists of five standards: 0 ng, 0.1 ng, 0.2 ng, 0.5 ng and 1.0 ng. The volumes of working standard solution required to achieve the five standard concentrations are shown in Table 1.

Table 1. Volumes of Working Standard Required to Generate Aqueous Standards

Hg Delivered to Trap	Volume of Hg Standard
0 ng	0 mL
0.1 ng	0.05 mL
0.2 ng	0.10 mL
0.5 ng	0.25 mL
1.0 ng	0.50 mL

Standards for the calibration curve are generated starting with the zero point (0 mL of working standard solution) and continued in ascending order to the highest volume, usually 0.50 mL of working standard solution. First, a blanked gold-coated bead trap is attached to the end of the soda lime trap. Then 1.0 mL of SnCl_2 is added to the standard bubbler followed by the appropriate volume of working standard solution. The standard bubbler is quickly attached to the impinger and the solution is purged at 450 cc/min for 5 minutes. The gold-coated bead trap is analyzed immediately after purging.

After each of the standards for the calibration curve has been analyzed, a linear regression is calculated to establish the coefficient of determination (r^2), the slope of the line and how well the slope of the curve predicts each of the points in the calibration curve. The 0 mL standard area is subtracted from each of the other points which are then regressed against the expected values using no intercept (line is forced through zero). The r^2 must be >0.995 and each of the points on the curve must be predicted by the slope within 10% of their true value (Table 2). If these criteria are not met, specific points which are errant are repeated and the linear regression recalculated.

Table 2. Example Calibration Curve and Calculation of Slope

Standard (ng Hg)	Response (AU)	Response (AU)- Zero Point (AU)	Predicted Value (ng Hg)
0	56,714	0	0
0.100	1,364,600	1,307,886	0.103
0.200	2,571,000	2,514,286	0.199
0.500	6,357,800	6,301,086	0.498
1.000	12,709,000	12,652,286	1.001

Slope = 7.909E-8 ng/AU

Slope⁻¹ = 12,643,823 AU/ng

r² = 0.9999

This curve is accepted and sample analysis commences.

Control standards are analyzed every sixth sample. The control standards are generated in the same manner as described above and are chosen to be representative of the samples being analyzed. The integrated area from each of the control standards must be within 10% of the slope of the calibration curve in order to continue analyzing. If this is not the case, a second control is analyzed immediately. If the second control indicates that analyzer sensitivity has changed a second calibration curve is generated and sample analysis is continued.

3.3.5 Calculation of Mercury Concentration

Mercury concentration in precipitation is calculated in ng/L. The total reagent blank response is subtracted from the analytical aliquot response and the difference is multiplied by the slope of the calibration curve which is in ng/AU. The mass of Hg for the entire sample is then calculated by dividing the analytical aliquot Hg mass by the analytical aliquot volume and multiplying the result by the total volume of sample. Once the ng of mercury in the entire sample is determined, the concentration is then adjusted for the (i) Teflon sample bottle blank, (ii) HCl preservative blank, (iii) HCl preservative dilution factor and finally converted to ng/L for reporting purposes (Table 3). The Hg concentration is calculated using Eqn. (1).

$$(1) \quad \text{Hgpcp} = \{(\text{CAU} \times \text{Slope} \times \text{TV}/\text{AV}) - (\text{AB} + \text{BB})\} \times (1000/\text{PV})$$

where:

Hgpcp = Hg concentration in precipitation (ng/L)

CAU = Total reagent blank corrected sample area units

Slope = Slope of the five point calibration curve (forced through zero)

TV = Total volume of sample (precipitation volume + HCl volume)

AV = Volume of analytical aliquot

AB = HCl acid preservative blank

BB = Mean Teflon sample bottle check blank

PV = Volume of precipitation collected

Table 3. Calculation of ng Hg/L in a Precipitation Sample.

1. Calculation of ng of mercury recovered from the analytical aliquot
$\text{ng Hg} = (\text{sample response (AU)} - \text{total reagent blank (AU)}) * \text{slope of calibration curve (ng/AU)}$ $(8,657,600 - 74,543) * 7.909\text{E-}8 = 0.679 \text{ ng Hg}$
2. Calculation of ng of mercury for total sample volume
$\text{ng Hg} = (\text{ng Hg from analytical aliquot} * \text{total volume of sample}) / \text{volume of analytical aliquot}$ $(0.679 \text{ ng Hg} * 439 \text{ mL}) / 100 \text{ mL} = 2.980 \text{ ng Hg}$
3. HCl acid preservative blank and Bottle blank correction
$\text{ng Hg} = \text{ng Hg for total sample volume} - (\text{HCl acid blank} + \text{Bottle blank})$ $2.980 - (0.004 + 0.020) = 2.956 \text{ ng Hg}$
4. Conversion to ng Hg/L
$\text{ng Hg/L} = \text{ng Hg for total sample volume} * (1000 / \text{precipitation volume collected})$ $2.956 * (1000 / 419) = 7.1 \text{ ng Hg/L}$

3.3.6 Trouble-Shooting

- A source of irreproducible results may be due to faulty gold-coated bead traps. These traps are numbered with discrete identifiers. Contact with halogen fumes, organic fumes or overheating of the trap during analysis can damage the trap, rendering it unusable. If performance of a gold trap is suspect, at least two consecutive standards are analyzed from this trap to determine its ability to amalgamate and release mercury.
- If a low response is observed, the impinger assembly is checked for leaks. Teflon compression fittings on the soda lime trap and the Teflon nut on the Teflon stopcock are the most common location of leaks.
- If peak-broadening is observed or no peak is detected in a sample, the analytical train is checked for leaks. Peak broadening is often the result of low gas flow, water vapor on the gold-coated bead trap, inadequate heating of analytical trap or an analytical trap damaged by exposure to halogen fumes or overheating. Analytical traps are replaced only when a potential problem is suspected with the trap.
- If the baseline drifts more than 10% the UV lamp is replaced. After replacement, the analyzer is allowed to equilibrate for 24 hours. If the problem persists,

sources of power fluctuation sources, drafts or air currents that may be changing the temperature of the UV lamp are investigated.

- Room temperature in which the CVAFS is located is maintained between 20-22°C, however, if the temperature exceeds 26°C analysis is stopped, since instrumental noise increases significantly.

4.0 Performance Criteria, Quality Assurance and Quality Control

- 4.1 Field operators are carefully instructed in the techniques of contaminant-free precipitation sample collection for mercury determination. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network and are experienced with other precipitation collectors.
- 4.2 Every 6 months UMAQL personnel inspect each of the sampling sites to audit the performance of the equipment and to make all necessary repairs or adjustments.
- 4.3 Co-located samples are collected from three sampling sites during the study to quantify method precision. Reported concentrations for co-located samples are based on the mean of the two samples.
- 4.4 In order to confirm that the collection funnel assemblies are free of mercury, funnel blank samples are collected throughout the study.
- 4.5 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 15% is maintained for samples with values at least 3 standard deviations greater than the detection limit. Analysis of standards and controls is within 10% of the stated value.
- 4.6 A minimum of 25% of all samples are analyzed in duplicate. Reported concentrations will be based on the mean of the replicates. Analytical precision averages better than 7%.
- 4.8 Every 3 months maintenance on the CVAFS analyzer is conducted, including replacement of the UV lamp, the Teflon tubing, and the detection cell.
- 4.9 The analytical trap is not changed unless it begins to demonstrate poor recovery or release of amalgamated mercury.
- 4.10 Teflon sleeves heat-sealed onto the gold trap are replaced frequently to maintain a gas tight seal.

5.0 Clean Room Procedures

- 5.1 Entering the Clean Room

Shoes are taken off outside the clean room by all UMAQL personnel. Personnel then enter the

outer vestibule (changing room). Once inside, the hood is put on followed by the clean room suit and clean room boots. The boots are snapped to the suit at the back of the leg (to hold up the boots) and are buckled in the front. Personnel then step over a dividing bench where they put on clean room gloves and snap the clean room suit at the wrist. Now fully clothed they enter the clean room making sure to securely close the door behind.

5.2 Taking Supplies into the Clean Room

All supplies to be taken into the clean room are double bagged in polyethylene. The supplies to be taken into the clean room are placed in the outer dressing room. Upon entering the clean room, the outer bag is removed and left in the entry room. All supplies that enter the clean room that have not been bagged are rinsed with MQ-water and wiped off with particle-free wipes.

Appendix A: Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation, sample collection and sample analysis that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

- Class 100 Clean Room, Work Stations
- Clean Room Gloves
- Particle-free Wipes
- Clean Room Cap, Gown and Boots
- Milli-Q Water (18.2MΩ/cm)
- Exhaust Hood
- Acetone
- Alconox
- Polyethylene Tubs
- EM Science Tracepur and Suprapur Hydrochloric Acid
- Polytherm Water Bath (Science/Electronics)
- Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
- New Polyethylene Bags
- 20 Liter Polyethylene Carboys

2. Sample Collection

- MIC-B Wet-Only Precipitation Collector (MIC)
- UMAQL Modified Acrylic Insert
- Digital Indoor/Outdoor Recording Thermometer
- BSG Collection Funnels
- Polypropylene Collection Funnels
- Teflon & Polypropylene Precipitation Adapters
- Glass P-trap Vapor Lock
- 1 Liter Teflon & Polypropylene Sample Bottles
- Funnel Heat Tape Nests & Variable Transformer
- Ceramic Space Heater
- 2 Gallon HDPE Bucket
- Particle-Free Gloves
- Teflon Tape
- Sample Labels
- Permanent Label Markers
- Field Operator Log Book
- Shipping Crates

3. Sample Analysis

- Cold Vapor Atomic Florescence Detector (Brooks Rand, LTD.)
- Line Tamer/Conditioner (Shape Magnetronics Model PCLT 150)
- Integrator (Hewlett-Packard Model 3390A)
- Helium, Ultra High Purity Grade (99.999%)
- Mass Flow Controller (Tylan)
- Nichrome Coils (UMAQL)
- Electric Leads
- Variable Transformers (Staco Energy Products Co. Type 3PN1010)
- Cooling Fans
- Gold-Coated Glass Bead Traps (UMAQL)
- Pre-purified (99.998%), Analyzed Nitrogen
- Glass Impingers
- Resin-coated Ring Stand
- 100 mL Graduated Glass Bubbler
- 12.7 cm lengths of 1.27 cm OD Glass Tubing (Soda Lime Trap)
- Automatic Pipettes
- Teflon Reagent Bottles (Clear and Opaque)
- Teflon Reagent Vials
- Resin-coated Wire Rack (Support Bubbler)
- Refrigerator